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WATER QUALITY BASIC DATA. REPORT ON ANALYTICAL REFERENCE SAMPLE TYPE I, BD-3

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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water quality basic data

report on analytical reference sample

TYPE I, BD-3

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SANITARY ENGINEERING CENTER

Cincinnati, Ohio

Participants in Study of Type I - BD-3
(Distributed Sept. 23, 1958)

Yankton Water Department
Yankton, South Dakota

East St. Louis Water Co.
East St. Louis, Illinois

Cairo Water Company
Cairo, Illinois

City Water Department
Cincinnati, Ohio

North Augusta Water Dept.
North Augusta, South Carolina

Board of Water Commissioners
Water Works Park Filtration Plant
Detroit, Michigan

East Liverpool Water Department
East Liverpool, Ohio

Chemical-Toxicological Laboratory
Louisiana State Health Dept.
New Orleans, Louisiana

Torresdale Laboratory
Philadelphia Water Department
Philadelphia, Pennsylvania

Metropolitan Utilities District
Omaha, Nebraska

Corps of Engineers
Dalecarlia Filtration Plant
Washington, D. C.

Massachusetts State Dept. of Health
Lawrence Experiment Station
Lawrence, Massachusetts

Crown Zellerbach Corporation
Central Research Dept.
Camas, Washington

International Business Machine
Corporation
Poughkeepsie, New York

School of Engineering
Washington State College
Pullman, Washington

City Water Department
Williston, North Dakota

Minneapolis-St. Paul Sanitary
District
St. Paul, Minneapolis

Dubuque Water Department
Dubuque, Iowa

Boulder City Water Plant
Boulder City, Nevada

Arizona Water Company
Yuma, Arizona

Burlington Water Department
Burlington, Iowa

City of Memphis
Light, Gas & Water Div.
Memphis, Tennessee

Grand Junction Water Dept.
Grand Junction, Colorado

St. Joseph Water Company
St. Joseph, Missouri

City Water Department
Laredo, Texas

Hagerstown Water Department
Hagerstown, Maryland

Participants (con't)

Water, Gas & Sewage Treatment Dept.
Duluth, Minnesota

City of St. Louis Water Dept.
St. Louis, Missouri

St. Louis County Water Company
University City, Missouri

Huntington Water Corp.
Huntington, West Virginia

City Water Company
Chattanooga, Tennessee

Tennessee Valley Authority
Stream Pollution Control Laboratory
Chattanooga, Tennessee

Easton Pennsylvania Water Dept.
Easton, Pennsylvania

City Water Department
Denison, Texas

Mississippi State Board of Health
Chemical Laboratory
Jackson, Mississippi

Weiser Water Department
Weiser, Idaho

Bismarck Water Department
Bismarck, North Dakota

N. Dakota State Dept.of Health
Public Health Laboratory
Bismarck, North Dakota

Evansville Water Dept.
Evansville, Indiana

City Water Department
Pasco, Washington

INTRODUCTION

Much of the physical and chemical data accumulated by the PHS National Water Quality Network are the result of the cooperative efforts of many laboratories located at or near the sampling sites. Because these analyses originate from so many different sources, it is essential that they be comparable as to accurary. The reference sample technique is a mechanism by which this objective can be achieved. Reference samples are being submitted periodically to each of the cooperating laboratories to insure continued accuracy of the data submitted.

REPORT ON THE ANALYTICAL REFERENCE SAMPLES TYPE I, BD-3

Sample Type I, BD-3 is the third in a series of standard samples representative of the mineral analyses being reported to the Water Quality Program. Thirty-seven laboratories received this sample and 35 have reported in time to have their results included in this report. Most laboratories have little or no difficulty in performing these examinations, as comfirmed by the general excellence of the reported results.

The individual analyses are presented in Table II and the bar graphs. The dotted lines on the graphs represent limits of accuracy for this sample which are acceptable to the Program. The selection of these limits was influenced by the accuracy with which each test can be performed, as determined by "Standard Methods" as well as the needs of our program. In most cases, those laboratories falling outside the acceptable range were notified immediately and requested to review the procedures used in order to determine the reasons for the discrepencies.

It is strongly urged that all cooperating laboratories furnish comments on the analytical methods used. A complete log of pertinent details, difficulties, modifications, sources of error, and other factors affecting the precision and accuracy of the analytical procedures would be extremely valuable in the development of simpler and more accurate analytical procedures. This report may also be useful as a means of self-evaluation by each of the participating agencies. Assistance on laboratory procedures is available to the cooperating laboratories from the Public Health Service, through its Regional Offices or the Sanitary Engineering Center.

DISCUSSION OF RESULTS

Statistical comparisons in this report were developed from the deviations from known quantities added to the sample. The range of deviations considered acceptable to the program were based on the precision and accuracy values as presented in "Standard Methods" for the various tests involved. Table I, below, is a summary of the expected accuracy for the various tests from "Standard Methods" and the ranges acceptable for the Water Quality Network for this reference sample.

Laboratories reporting values outside the range of acceptability should investigate their procedures for sources of error. Have standard solutions been checked recently? Are the reagents too old? Are sample sizes adequate for maximum accuracy? How carefully are weighings being made? Are standard curves being checked frequently? Although most of these tests are simple and "routine", a thorough review of the details in each procedure may disclose errors which have become habitual and escape unnoticed during routine operations.

TABLE I

Acceptable Limits of Accuracy

	Standard Methods	Water Quality Program
Chloride 100 ml sample	± 1.0 mg/l	± 2.0 mg/l
Sulfate Turbidimetric	± 10%	± 10%
Alkalinity 50 ml sample	± 2.0 mg/l	± 4.0 mg/l
T.D.S. 200 ml sample	3 mg/l	13 mg/l
Hardness 50 ml sample	± 2 mg/l	± 3.1 mg/l
pH	± 0.1 unit	± 0.2 unit
Turbidity	-	± 26 units

The Tenth Edition of "Standard Methods" gives the expected precision and accuracy for each test, within the range of concentration normally encountered in water analysis. These "standards of accuracy" should be attainable by most laboratories performing these routine examinations. The additional errors, allowable for the Network Program, are intended only as a guide to the cooperating laboratories and are not to be considered as the ultimate goal in the achievement of laboratory accuracy. The limits allowed in this report are narrower than those allowed in previous reference samples, and they will continue to be revised upward as more and more laboratories continue to improve their performance through experience gained in the Program.

CHLORIDE - 15 mg/l

Although several methods are available for this determination, 20 or 32 laboratories used the Mohr procedure. The most frequent criticism of this method is the obscurity of the real endpoint due to the presence of the Silver Chloride precipitate. A frequent, but minor error is failure to correct for the indicator blank. The use of a yellow light aids in detecting the endpoint. The chief precaution to be observed in this determination, as in any volumetric procedure, is standardization of reagents. Eighteen of the 32 laboratories reporting this analysis fell within 2 mg/l of the known value. Ten additional laboratories fell within 3 mg/l and half of the reported results were within ± 1 mg/l of the known value. It is evident that most laboratories can easily perform the chloride determination within the limits of precision.

SULFATE - 33 mg/l

Eleven of the 24 laboratories reporting this analysis fell within ±10% of the known value. Six additional laboratories fell within 20%. Of the laboratories outside the acceptable range, one reported using the Tetrahydroxyquinone (THQ) procedure; one reported using the turbidimetric procedure; and five reported using the gravimetric procedure.

At higher sulfate concentrations, the gravimetric procedure is considered to be the more accurate, but at the concentration present in this sample the turbidimetric procedure appears to be equally satisfactory. The turbidimetric procedure has the advantages of being less time consuming and more simple to perform.

On this particular sample, using either Turbidimetric or gravimetric procedures, it was necessary to remove the turbidity prior to sulfate precipitation. If this operation was not properly performed, a high result would be obtained. The usual precautions of washing and drying precipitates also had to be observed to obtain good results on the gravimetric procedure.

TOTAL DISSOLVED SOLIDS - 134 mg/l

In the performance of the Total Dissolved Solids determination, no difficulties should normally be encountered. A measured volume of turbidity-free sample is placed in a dish, evaporated to dryness and weighed. Two precautions must be observed: (1) the turbidity must be completely removed, and (2) the sample must be taken to dryness at 103-105°C. Incomplete drying allows excessive amounts of water to be included in the final weighing which, along with turbidity particles, will cause high results. A third precaution, also related to drying, must be exercised. If the drying temperature is too high, certain materials, such as carbonates, bicarbonates, or chlorides may be partially volatilized and the result will be too low. For these reasons the precautions, while simple, must be strictly observed. The size of sample taken for this test will influence its precision considerably, particularly with waters of low solids content such as this sample. To achieve a satisfactory result the sample size should be large enough to produce a residue weighing not less than 25 mg in order that the precision of the weighing fall within the acceptable range.

Of the 20 laboratories reporting this determination, 15 fell with the 13 mg/l range and at least half of the results were within 9 mg/l.

By referring to the bar graph for this analysis, it can be seen that the grossly erroneous results are on the high side with the exception of one which seems to be an arithmetical error. A probable cause for these errors would be incomplete removal of turbidity particles or too small sample size. A very retentive filter, preferably a millipore, is required for complete removal of turbidity.

ALKALINITY - 73 mg/l (as $CaCO_3$)

The initial Type I, BD-3, sample, subsequent to shipment, was found to be unstable with respect to pH and Alkalinity. Because of this instability, no specific values could be assigned for these determinations. Subsequently a special sample with a

higher buffer capacity was prepared and distributed. The results obtained from analysis of the special sample are the ones used in this report.

This procedure allows a choice of indicators or electrometric measurement for the detection of the endpoint. Of the 32 laboratories reporting this analysis, 11 used methyl orange indicator; four used methyl purple; one used methyl green; five used a pH meter or automatic titrator; and one used Cooper's mixed indicator. The other 10 laboratories did not report the method used. Half of the reported results were within 2 mg/l. Of the eight laboratories outside the acceptable range, three reported using methyl orange; two used methyl purple; one used the electrometric endpoint; and the others did not indicate the method of analysis. It is of interest that of the five laboratories using an electrometric endpoint, four used the endpoint at pH 4.6 and obtained results that deviated from the known value by 0, 0, 1, and 4 mg/l. The other analyst used an endpoint at pH 4.3 and, obtained a result that was 5 mg/l too high.

HARDNESS - 31 mg/l (as $CaCO_3$)

All laboratories employed some modification of the EDTA titration procedure. One laboratory also reported a parallel titration by the Soap method which did not agree with the known value. Fourteen of the 35 laboratory results fell within 3.1 mg/l of the concentration added to the sample. Ten additional laboratories fell within 6.2 mg/l of the known value. One half of the results were within 4 mg/l of the known concentration. This titration presents no great difficulty as the endpoint is easy to detect, provided that the indicator, Eriochrome Black T, is in good condition. This may be assured by using the indicator in dry form, mixed with sodium chloride. Errors may have been due to improperly standardized reagent, miscalculation, or faulty indicator.

HYDROGEN ION CONCENTRATION (pH) 7.3

The results listed under this determination were those reported for the special sample refered to under Alkalinity.

The sample was made from a Clark and Lubs buffer and the pH was verified at the SEC by averaging the results from three carefully standardized pH meters. Of the 32 laboratories reporting this analysis, 30 fell within ± 0.2 units of the known value.

At least half of the results were within ± 0.1 units of the true value. Of the two results outside of the acceptable limit, one had a deviation of 0.4 units and this was obtained by the use of a comparator rather than a pH meter. The other laboratory later reported that its pH meter was defective. "Standard Methods" indicates that a precision of 0.1 pH unit is readily attainable with the glass electrode.

TURBIDITY - 130 Jackson Units

The turbidity value assigned to this sample was obtained by a series of readings on the Jackson Candle Turbidimeter following a period of aging after the sample was prepared. The original value of 150 units added to the sample was reduced to 130 units after a week aging period. This value then persisted at 130 for a period of two months, showing no further evidence of agglomeration.

Of the 34 laboratories reporting this analysis, 19 fell within 26 units of the known value and at least half were within 23 units. The majority of the deviations still tend to be on the low side, which suggests the possibility that insufficient shaking of the sample might be the cause of the error. Another source of error may be the conversion to Jackson units when instruments other than the Jackson Candle turbidimeter are used. Of the 15 laboratories outside of the acceptable range of error, four reported the use of the Jackson Candle turbidimeter; and one used a colorimeter. The remainder reported using a turbidimeter other than the Jackson Candle apparatus, except for the single laboratory that had a gross error on the high side and did not report the method of analysis.

TABLE II - SUMMARY OF RESULTS

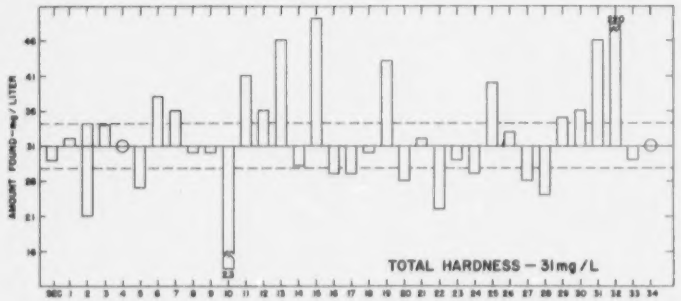
ANALYTICAL REFERENCE SAMPLE TYPE I, BD-3

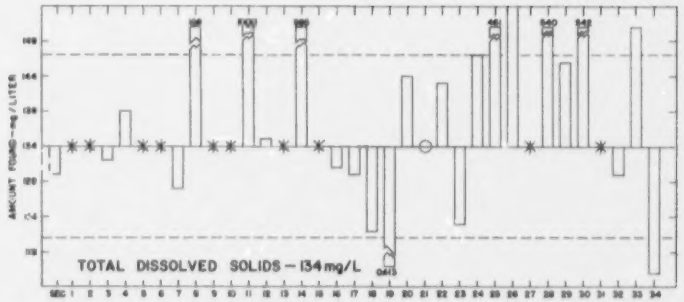
Analyses Performed	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount Added	15 mg/l	33 mg/l	134 mg/l	73 mg/l	31 mg/l	7.3	130
Lab #	Average Amount Reported by Each Lab						
SEC	15	33	130	73	29	7.3	130
1	12			70	32	7.1	84
2	18			68	21	7.3	110
							120
3	15	35	132	71	34	7.4	76
4	20	36	139	76	31	7.2	103
5	16			72	25	7.1	132
6	17			73	47(1)	7.3	170
					32(2)		
7	16	24	128	72	36	7.4	125
8	21	38	158	73	30	7.3	102
9	17			74	30	7.5	96
10	4			7	2	7.1	74
11	17	32	1000	70	41	7.5	148
12	16	38	135	73	36	7.2	117
13	15				46		84
14	18	30	585	85	28	7.2	68
15	17				49		54
16	19	35	131	78	27	6.3	107
17	16	26	130	71	27	7.4	150
18	15	176	122	81	30	7.3	148
19	17	38	0.4	78	43	7.2	51
20	15	38	144	72	26	7.4	111
21	18	35	134	76	32	7.3	155
22	16	45	143	71	22	7.5	115
23	16	36	123	73	29	7.2	148
24	15	34	147	70	27	7.1	97
25			461	71	40	7.4	121
26	15	34	154	69	33	7.2	123
27	16			(72)	26	(7.4)	
				109		7.2	
28	16	15	540	72	24	7.4	138
29	16	35	146	70	35	7.2	58
30	20	37	542	72	36	7.2	100
31	3			94	46	6.9	75
32	17	56	130		220		118
33	14	37	157-145	74	29	7.2	123
34	16	41	116	70	31	7.2	123
35	20	52		76	17	7.2	127

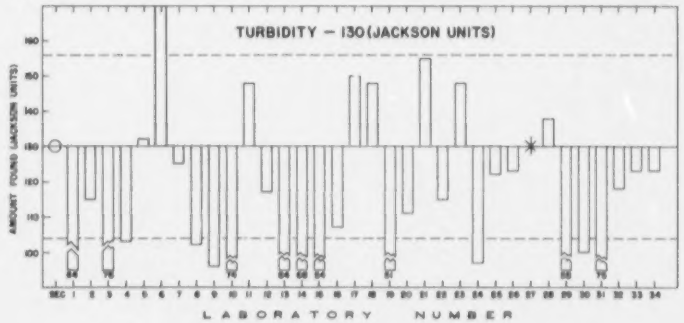
(1) soap
(2) EDTA

WATER QUALITY BASIC DATA

ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-3







NOTE:
○ - PERFECT RESULTS
✳ - NO ANALYSIS PERFORMED

WATER QUALITY BASIC DATA

ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-3